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Nitration of Adamantane and Diamantane with Nitronium Tetrafluoroborate[1]

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Abstract: The slow reaction of adamantane with nitronium tetrafluoroborate at room temperature in purified, nitrile-free nitromethane or in nitroethane gives 1-nitroadamantane in 66% and 74% isolated yield, respectively. Similar reaction of diamantane gives 62% 1- and 5% 4-nitrodiamantane. Initial reaction upon aqueous workup gives 1-adamantanol with 1-fluoroadamantane, 3-fluoro-1-adamantanol, and adamantanone as byproducts. Upon prolonged reaction 1-nitroadamantane is formed in good yield. The experimental data are in accord with intermediate formation of the 1-adamantyl cation (by hydride abstraction or cleavage of initially formed 1-nitroadamantane) followed by reaction with HNO_2 or NO_2^- formed in the reaction, giving 1-adamantyl nitrite, which then undergoes cleavage–rearrangement to give 1-nitroadamantane. A small kinetic hydrogen isotope effect of $k_H/k_D = 1.2–1.3$ is indicative of a nonlinear highly unsymmetrical transition state in the rate-determining step of the reaction.

Introduction

Several reports have appeared on attempted nitration of adamantane. Stetter's review[2] stated that adamantane is not attacked by concentrated nitric acid even under severe conditions. Smith and Williams[3] found that adamantane did not react with 20% nitric acid at 130 °C. However, heating a solution of adamantane and nitrogen dioxide in carbon tetrachloride at 140–160 °C gave nitroadamantane, as well as chloroadamantane derivatives. Reaction of adamantane with concentrated nitric acid in glacial acetic acid at 140 °C also gave nitroadamantane along with some minor oxidation products. Schneider and co-workers[4] found that passing NO_2 through solutions of alkyladamantanes at elevated temperatures (~200 °C) led to mixtures containing 1-hydroxy-, oxo-, 1-nitro-, 1-nitrooxo-, 1-nitrohydroxy-, and 1,3-dinitroalkyladamantanes.

Olah and Lin[5] reported nitration of adamantane with nitronium salts in aprotic solvents at ambient temperature but obtained only 10% yield. Moiseev and co-workers[6-9] observed formation of 1-adamantyl nitrate (and 1-hydroxyadamantane) in the reaction of adamantane with nitric acid. Vodicka et al.[10] obtained 1-nitroadamantane as a minor product when optimizing the yield of 1-adamantanol from the reaction of adamantane with bromine in nitric acid.

Yoshida et al.[11] carried out the nitration of adamantane under free radical conditions by irradiating a solution of adamantane and N_2O_5. Adamantyl nitrate, 1-nitroadamantane, 2-adamantanone, and 2-nitroadamantane were obtained in a 5.5:4.4:2.2:1 ratio.

Umstead and Lin[12] found that 1-nitroadamantane and 1-adamantyl nitrite were formed in the photoinduced reaction of adamantane with N_2O_4 in carbon tetrachloride.

Following our earlier report[5] of the limited (10%) nitration of adamantane with nitronium salts, we embarked upon a more detailed study including that of the mechanism of the reaction.

Results and Discussion

In the study of the reaction of adamantane with nitronium tetrafluoroborate we were frustrated for a long time by low yields and the predominant formation of products other than the desired 1-nitroadamantane. Among several solvents tried (including sulfolane, acetonitrile, chloroform, methylene chloride, etc.), only in nitromethane was meaningful nitration observed, but the consistent major product of the reaction was *N*-adamantylpropionamide. This was found (*vide infra*) to be the consequence of the presence of ~5% propionitrile in commercial nitromethane. When adamantane was added to a stirred suspension of nitronium tetrafluoroborate in dry, freshly distilled (over CaH_2), commercial nitromethane and the mixture was stirred at ambient temperature under a dry nitrogen atmosphere for up to 4 days, aqueous workup and analysis by GC-MS gave at least seven products with only 17% 1-nitroadamantane (see Table I). The 17% yield of 1-nitroadamantane is only a modest improvement over the previously reported 10%.[5] *N*-1-Adamantylpropionamide (58.1%) is the major product, together with 1-adamantanol (9.6%) as well as 1-fluoroadamantane, 3-fluoro-1-adamantanol, 1-adamantyl isocyanate, adamantanone, and *N*-1-adamantylacetamide as minor byproducts. These products are derived from S_N1 reaction of the intermediately formed 1-adamantyl cation with nucleophiles present in the system or upon aqueous workup. 1-Adamantanol is also formed upon aqueous workup from adamantyl nitrite. As hydride abstraction from adamantane by $NO_2^+BF_4^-$ results in the formation of the 1-adamantyl cation and HNO_2, nitrite ion is formed in the system as the reaction progresses. It will react with the 1-adamantyl cation to give 1-adamantyl nitrite and 1-nitroadamantane, respectively. Its concentration initially is, however, very low and only builds up

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Table I. Reaction of Adamantane with Nitronium Tetrafluoroborate

product	yield (%)[a] in commercial CH_3NO_2[b]	 in nitrile-free CH_3NO_2	 in $CH_3CH_2NO_2$
1-nitroadamantane	17.4	66.2	74.0
1-fluoroadamantane	0.5	2	3.7
1-adamantanol	9.6	12.3	10.7
3-fluoro-1-adamantanol	1.2	2.5	9
adamantanone	0.2	0.4	0.1
1-adamantyl isocyanate	1.2		
N-adamantylacetamide	0.3		
N-adamantylpropionamide	58.1		
adamantane (unreacted)	5.9	16.6	11.5

[a] Isolated normalized yields based on adamantane. [b] Percentages do not add up to 100% because of additional unidentified minor products.

as adamantane is consumed. Previously Olah and Lin reported[13] that the reaction between 1-adamantyl hexafluoroantimonate and $AgNO_2$ in AsF_3 solution gave 1-nitroadamantane. Furthermore, a low yield of 1-nitroadamantane was also obtained along with 1-adamantanol and 1-chloroadamantane, when adamantane was reacted with tetrabutylammonium nitrite in methylene chloride solution in the presence of aluminum chloride.[14] The reaction of the ambident nitrite ion also gives adamantyl nitrite which can, however, reenter the reaction cycle (*vide infra*). A referee further suggested that reaction of HNO_2 (formed by hydride abstraction) with NO_2^+ would give $ONONO_2$, which could preferentially react with the 1-adamantyl cation to give 1-nitroadamantane.

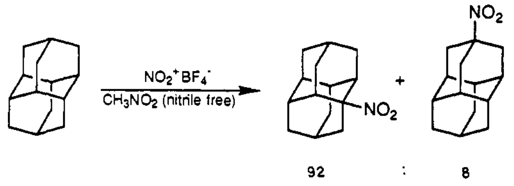
Adamantanone is formed by oxidation of 2-adamantanol. The obtained amides are the products of Ritter reaction of the 1-adamantyl cation with acetonitrile and propionitrile present in commercial nitromethane in approximately 1% and 5%, respectively.[15a] Indeed Bach et al. reported previously that adamantane with $NO_2^+BF_4^-$ in acetonitrile solution gave *N*-1-adamantylacetamide.[16] In control experiments we found that the reaction of 1-adamantanol with nitronium tetrafluoroborate in commercial nitromethane, after workup, gave the same amides. Neither 1-adamantanol nor 1-nitroadamantane was, however, formed when *N*-adamantylpropionamide was reacted with nitronium tetrafluoroborate in nitromethane. Amides are not formed until the aqueous quenching of the reaction mixture. Shaking an aliquot from the nitration reaction mixture with acetonitrile followed by aqueous workup gave mostly *N*-adamantylacetamide and only a very small amount of the corresponding propionamide.

Having found the effect of impurity nitriles in commercial nitromethane on the reaction of adamantane with nitronium tetrafluoroborate, we carried out the reaction in dry, nitrile-free nitromethane. When carefully purified nitrile-free nitromethane was used as solvent, 1-nitroadamantane was obtained in 66% isolated preparative yield (after column chromatography over silica gel) but only after prolonged (4–7 days) reaction time. No significant formation of nitroadamantane is observed in the monitored reaction for up to 2 days, and upon aqueous workup 1-adamantanol was the major product besides *N*-1-adamantylpropionamide.

Commercial nitroethane, in contrast to nitromethane, is free of nitriles,[15b] and when it was used as solvent under conditions similar to those above, 1-nitroadamantane was obtained in 74% yield together with 1-adamantanol, 3-fluoro-1-adamantanol, and 1-fluoroadamantane as minor products (Table I).

When the reaction of adamantane with 2 equiv of nitronium tetrafluoroborate was carried out faster consumption of adamantane was observed but there was no evidence of any dinitroadamantane formation. The reaction mixture gave, after column chromatography, 1-nitroadamantane in only 38% yield. The complexity of the reaction lies in the nitrolysis (not unlike protolysis) of the $C-NO_2$ bond of 1-nitroadamantane (*vide infra*). The reaction of 1-nitroadamantane with 1 equiv of nitronium tetrafluoroborate in nitroethane gave 1-adamantanol and 1-fluoroadamantane at the expense of 1-nitroadamantane. A 2-mol excess of nitronium tetrafluoroborate in 1 h resulted in the quantitative consumption of nitroadamantane. Upon aqueous workup 1-adamantanol and 1-fluoroadamantane were obtained with a minor amount of adamantanone.

Diamantane was also reacted with nitronium tetrafluoroborate (1 molar equiv) in nitrile-free nitromethane to give a mixture (92:8) of two nitrodiamantanes in 67% isolated yield. A pure sample of the major product was obtained by a careful chromatographic separation and identified as 1-nitrodiamantane on the basis of its spectral (NMR) properties.[17]



The reaction of diamantane with 2 equiv of nitronium tetrafluoroborate again resulted in a decrease in the yield of mononitrodiamantane to 32% and a complex product mixture with no indication of dinitrodiamantane.

In order to gain additional information on the mechanism of the reaction of nitronium tetrafluoroborate with adamantane, the kinetic hydrogen isotope effect, k_H/k_D, of the reaction was determined. In a competitive intermolecular experiment pure nitronium tetrafluoroborate (less than 0.5 equiv as the limiting reagent) was reacted with an equimolar mixture of adamantane and 1,3,5,7-tetradeuterioadamantane in purified nitromethane. After workup the products were analyzed by GC-MS. k_H/k_D was found on the basis of the ratio of the nitro products to be 1.31 ± 0.05. A similar experiment with dry nitroethane as a solvent gave $k_H/k_D = 1.30 \pm 0.05$.

We also studied the kinetic hydrogen isotope effect via intramolecular nitration of 1-deuterioadamantane with pure nitronium tetrafluoroborate in nitroethane solvent. After workup, the products as analyzed by GC-MS gave an isotope effect of $k_H/k_D = 1.20 \pm 0.05$

All previous studies[18–29] showed that only a small isotope effect is expected when the transition state of an electrophilic reaction

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[15] (a) Boiling points of nitromethane and propionitrile are 100. 8–101 and 97 °C, respectively; they appeared as a single peak in the chromatogram (DB-5 column, column temperature 35 °C, injection temperature 250 °C) of the GC-MS. The base peaks for propionitrile and nitromethane are 54 ($M^+ - 1$) and 61 (M^+), respectively. The percentage of propionitrile in nitromethane was determined by comparing the areas for the masses 54 and 61. (b) GC-MS analysis of nitroethane (W. R. Grace Co.) showed it to be free of nitrile impurities.

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[17] On a Fisher-Johns melting point apparatus, 1-nitrodiamantane slowly sublimed and at 200 °C sublimation was complete. On a Mettler FP1 apparatus the melting point was 237.9 °C. IR (KBr): 1529, 1358. ^{13}C NMR ($CDCl_3$): 90.36 ($C-NO_2$), 44.38 (CH_2), 39.18 (CH), 38.70 (CH), 37.34 (CH_2), 36.53 (CH_2), 35.80 (CH), 33.43 (CH_2), 28.53 (CH), 24.28 (CH). MS: 187 ($M - NO_2$, 100%), 131 (11%), 105 (15%), 91 (26%).[9]

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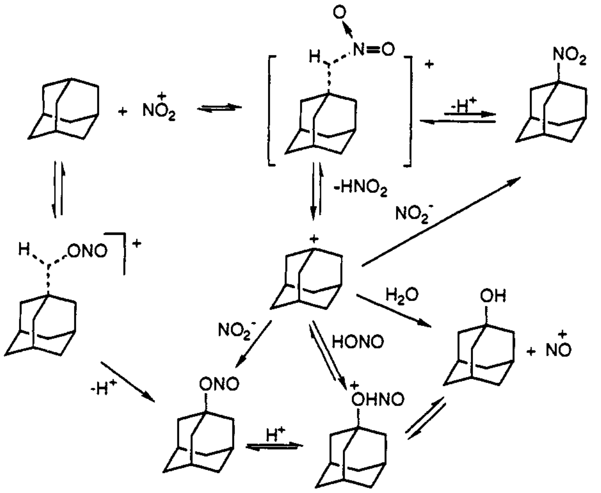
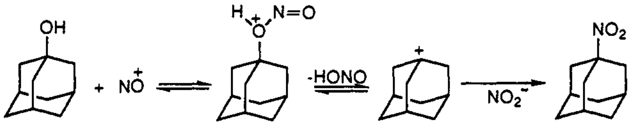
of a saturated system is nonlinear. In the presently studied nitration of adamantane with nitronium tetrafluoroborate the observed small isotope effects of k_H/k_D = 1.2–1.3 are in all probability primary in nature due to a nonlinear transition state in the rate-limiting step.

As little 1-nitroadamantane is observed during the first 18 h of the reaction of adamantane with $NO_2^+BF_4^-$, it may be considered that its formation by direct S_E2 nitration is reversible. Tertiary nitroalkanes are well known to cleave under acidic conditions. Indeed when 1-nitroadamantane was reacted with excess $NO_2^+BF_4^-$ (as well as with strong acids such as CF_3SO_3H or HF/BF_3), it was rapidly consumed, giving upon aqueous workup 1-adamantanol and 1-fluoroadamantane (as well as 1-fluoro-3-adamantanol). This shows that the tertiary C–N bond, not unexpectedly, can be cleaved under the initial reaction conditions leading either to the 1-adamantyl cation (and subsequent products) or can give back adamantane. In the hydride abstraction of adamantane by NO_2^+ to 1-Ad$^+$, the abstracted hydride forms HNO_2. As its concentration increases, NO_2^- formed in its ionization equilibrium increasingly can act as a nucleophile to give 1-nitroadamantane and 1-adamantyl nitrite. 1-AdONO could, however, also be formed directly from adamantane by the ambident attack of NO_2^+ reacting as an oxygen electrophile. The proposed mechanistic scheme thus is



That 1-adamantyl nitrite under the reaction conditions undergoes cleavage–rearrangement to 1-nitroadamantane, which is slowly building up in the equilibrium system as excess NO_2^+ is consumed, was substantiated when 1-adamantanol was reacted with $NO^+BF_4^-$ in nitroethane solution. After 2 days, 1-nitroadamantane (as well as minor amounts of 1-fluoroadamantane and 3-fluoro-1-adamantanol) was obtained.



Interestingly adamantane itself reacts with pure $NO^+BF_4^-$ (free of $NO_2^+BF_4^-$) slowly to form 1-nitroadamantane. The reaction of adamantane and $NO^+BF_4^-$ after 5 days gave 1-nitroadamantane and 1-adamantanol in a 1:1.2 ratio, whereas intially only 1-adamantanol (and some 1-fluoroadamantane) was observed. On prolonged reaction 3-fluoro-1-adamantanol was found to be an additional minor product. In the reaction initial hydride abstraction gives 1-ad$^+$ and HNO (which decomposes to N_2O and H_2O). Reaction with water (formed in the reaction) then yields adamantanol, which reacts with excess NO^+ to give adamantyl nitrite followed by cleavage–rearrangement to 1-nitroadamantane.

Single electron transfer (SET) nitration of adamantane by NO_2^+ is unlikely as the first ionization potential of adamantane to Ad$^+$ is high. As neither coupling products nor 2-nitroadamantane are observed and light or oxygen had no effect, a radical nitration pathway seems highly unlikely.

Conclusions

The nitration of adamantane with nitronium tetrafluoroborate gives 60–70% in preparative yield of 1-nitroadamantane. The mechanism of the reaction was studied. Data are in accord with the intermediate formation of the 1-adamantyl cation (by hydride abstraction or cleavage of initially formed 1-nitroadamantane as long as an excess of NO_2^+ is present). The observed small kinetic hydrogen isotope effect (k_H/k_D = 1.2–1.3) is indicative of an unsymmetrical, nonlinear transition state in the ionization step. The 1-adamantyl cation then reacts with HNO_2 and NO_2^- formed in the reaction (the concentration of which is building up as the reaction proceeds) to give 1-adamantyl nitrite and 1-nitroadamantane. 1-Adamantyl nitrite was shown to undergo cleavage–rearrangements to 1-nitroadamantane under the reaction conditions.

In contrast to electrophilic nitration of aromatics giving nitroarenes stable in acidic media, electrophilic S_E2 nitration of alkanes and cycloalkanes, such as adamantane, can readily reverse due to the ease of the cleavage of tertiary C–N bonds under the reaction conditions. This leads to a more complex reaction path involving S_N1 type reactions.

Experimental Section

Commercial nitromethane was obtained from Mallinckrodt, Fisher Scientific, and Aldrich and was dried by refluxing over CaH_2 overnight and then distilled from CaH_2 prior to use. Nitroethane was a gift from the W. R. Grace Co. Nitronium tetrafluoroborate was prepared from nitric acid (purified from nitrous acid with urea), HF, and BF_3. While using commercially obtained $NO_2^+BF_4^-$ (Aldrich) one must be aware of its nitrosonium tetrafluoroborate impurity (up to 15%). Adamantane (Aldrich) was sublimed before use. GC-MS analyses were carried out on a Finnigan INCOS-50 mass spectrometer. NMR spectra in $CDCl_3$ with Me_4Si as the internal standard were recorded on a Varian VXR-200 spectrometer.

Purification of Nitromethane. The procedure for the removal of propionitrile and acetonitrile from commercial nitromethane was based on the conversion of nitriles into aldehydes.[29]

The literature method was modified as follows. HCl gas was bubbled into an ice-cold solution of commercial nitromethane (1000 mL) containing absolute ethanol (50 mL) for 5 h. The highly acidic solution was stored in the refrigerator overnight and then white crystals of the iminoester hydrochloride were separated by filtration. The filtrate was washed with 5% aqueous sodium carbonate solution which was saturated with sodium chloride, dried ($MgSO_4$), distilled over solid sodium carbonate, and redistilled (over CaH_2).

General Procedure for the Reaction of Adamantane or Diamantane with Nitronium Tetrafluoroborate. Nitronium tetrafluoroborate (1.34 g, 10 mmol) and dry nitrile-free nitromethane or nitroethane (10 mL) were placed in a flame-dried 25-mL round-bottom flask equipped with a magnetic stirrer and a dry nitrogen inlet. To this slurry was added adamantane, diamantane, or deuterated adamantane (10 mmol) in one portion at 0 °C, and the reaction was stirred at ambient temperature. The reaction was slow, and it was monitored every 8–12 h by GC-MS. When no further increase in the yield of 1-nitroadamantane was observed (typically after 4 to 7 days), the reaction was quenched with water and

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washed sequentially with 5% $NaHCO_3$ (3 × 25 mL) solution and water. The aqueous layer was extracted with methylene chloride (3 × 25 mL) and dried ($MgSO_4$). The combined organic extracts were evaporated under reduced pressure, and the desired nitroadamantane was purified on a silica gel column (50 g) with hexane–methylene chloride (3:1 v/v) as eluant. All experimental results were those of duplicate runs, and the 1-nitroadamantane obtained was characterized by comparing it with an authentic sample.

Preparation of 1,3,5,7-Tetradeuterioadamantane. A solution of tri-*n*-butyltin chloride (1.2 g, 3.2 mmol) in ether (5 mL) was added to a slurry of lithium aluminum deuteride (0.42 g, 10 mmol) in dry ether (50 mL). Then 1,3,5,7-tetrabromoadamantane (2.0 g, 4.4 mmol) was added in one portion and the resulting mixture was refluxed under a dry nitrogen atmosphere for 24 h. The reaction was cooled to room temperature, quenched with D_2O (4 mL) slowly, poured into water (30 mL), and extracted with pentane (5 × 50 mL). The combined pentane extracts were washed with saturated NaCl solution and dried (Na_2SO_4) and then the solvent was removed under reduced pressure. Column chromatography on alumina (50 g) with hexane as eluant yielded pure 1,3,5,7-tetradeuterioadamantane (566 mg, 92%); mp 266–267 °C; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.81 (t, J_{C-D} = 21 Hz, C–D), 37.80 (s, CH_2); MS *m/e* EI 140 (*M*, 77). The deuterium content of the product by GC-MS showed it to be >95.5% adamantane-d_4.

Preparation of 1-Deuterioadamantane. Following the same procedure outlined above, 1-bromoadamantane gave the desired 1-deuterioadamantane: mp 202–203 °C; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.68 (t, J_{C-D} = 21 Hz, C–D), 28.31 (s, C–H), 37.63 (s, CH_2–CD), 37.76 (s, CH_2); MS *m/e* EI 137 (*M*, 100). The GC-MS analysis of the product showed the deuterium content to be >97%.

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